Description

SYSTEM FOR CONTINUOUS GROWING OF MONOCRYSTALLINE SILICON

Technical Field

[1] **Related Application**

[2] This patent application claims the benefit of U.S. patent application serial no. 10/789,638, filed February 27, 2004.

[3] The field of the invention generally relates to growing silicon crystals by the Czochralski (CZ) technique . In particular, the field of the invention relates to a system and method for continuous and rapid growing of ultra pure, high minority carrier lifetime mono-crystalline silicon based on improvements to the Czochralski method.

Background Art

[4] Referring to **Figures 1A** and **1B**, to be useful for the fabrication of semiconductor electronic components, silicon must be formed into a large (about 10 - 30 cm diameter), nearly perfect, single crystal, since grain boundaries and other crystalline defects degrade device performance. Sophisticated techniques are needed to obtain single crystals of such high quality. Referring to **Figures 1A** and **1B**, to be useful for the fabrication of semiconductor electronic components, silicon must be formed into a large (about 10 - 30 cm diameter), nearly perfect, single crystal, since grain boundaries and other crystalline defects degrade device performance. Sophisticated techniques are needed to obtain single crystals of such high quality. Referring to **Figures 1A** and **1B**, to be useful for the fabrication of semiconductor electronic components, silicon must be formed into a large (about 10 - 30 cm diameter), nearly perfect, single crystal, since grain boundaries and other crystalline defects degrade device performance. Sophisticated techniques are needed to obtain single crystals of such high quality. These crystals can be formed by either the Czochralski (CZ) technique or the float-zone (FZ) method.

[5] Referring to **Figures 1A and 1B**, in a conventional CZ technique, pieces of polysilicon are first melted in a fused silica crucible **100** in an inert atmosphere (typically argon) within a growth chamber **102** and held at a temperature just above 1412 degrees C, the melting point of silicon. A high quality seed crystal **101** with the desired crystalline orientation is then lowered through pull chamber **106** into the melt **122** while being rotated. The crucible **100** is simultaneously rotated in the opposite direction to induce mixing in the melt and to minimize temperature non-uniformities. A portion of the seed crystal is dissolved in the molten silicon to remove strained outer portions and to expose fresh crystal surfaces. The seed is then slowly raised or pulled from the melt **122** by a crystal pulling mechanism **108**. As the seed is raised, it cools and material from the melt adheres to it, thereby forming a larger crystal or ingot **103**. Under the carefully controlled conditions maintained during growth, the new silicon

atoms continue the crystal structure of the already solidified material. The desired crystal diameter is obtained by controlling the pull rate and temperature with conventional feedback mechanisms. In this manner, cylindrical, single crystal ingots of silicon are fabricated. The seed is then slowly raised or pulled from the melt **122** by a crystal pulling mechanism **108**. As the seed is raised, it cools and material from the melt adheres to it, thereby forming a larger crystal or ingot **103**. Under the carefully controlled conditions maintained during growth, the new silicon atoms continue the crystal structure of the already solidified material. The desired crystal diameter is obtained by controlling the pull rate and temperature with conventional feedback mechanisms. In this manner, cylindrical, single crystal ingots of silicon are fabricated.

[6] The seed is then slowly raised or pulled from the melt **122** by a crystal pulling mechanism **108**. As the seed is raised, it cools and material from the melt adheres to it, thereby forming a larger crystal or ingot **103**. Under the carefully controlled conditions maintained during growth, the new silicon atoms continue the crystal structure of the already solidified material. The desired crystal diameter is obtained by controlling the pull rate and temperature with conventional feedback mechanisms. In this manner, cylindrical, single crystal ingots of silicon are fabricated.

Disclosure of Invention

Technical Problem

[7] A problem in a conventional CZ process arises when a high temperature charge of molten silicon **122** is heated within a typical narrow diameter, high width, high aspect ratio crucible **100** by means of heater elements disposed around the vertical walls of the crucible. Driving heat though the crucible walls to heat the charge creates stress on the crucible and shortens its useful life. After each growth cycle, the molten silicon remaining in the bottom of the crucible solidifies and expands to such an extent that it can break the crucible. Thus, in a conventional CZ process the crucible is generally a single use item.

[8] The silicon must be continuously heated to remain molten in the crucible. Thus, referring to **Figure 1B**, in a conventional high aspect ratio, narrow diameter CZ crucible**100** with heaters **118** disposed around the vertical walls of the crucible, the temperature distribution though the melt is characterized by a high thermal gradient and large temperature difference between the hot walls of the crucible and the coolest spot at the center of the crystal in the solidification zone at the melt/crystal interface as shown at **109**. Consequently there is a significant radial temperature gradient and convection velocity gradient across the solidification zone at the melt/crystal interface and the region adjacent to the walls are driven to an undesirably high temperature with attendant excess convection current velocity and thermal perturbations. This condition is sub-optimal for maximized pull rate of high quality defect free crystal. In order to grow more, high quality silicon at a faster rate, a different crucible and heater design is needed that provides a uniform temperature distribution with minimized thermal

gradient and convection velocity gradient in the solidification zone at the crystal/melt interface **107**.

[9] Conventional CZ grown silicon differs from ideal monocrystalline silicon because it includes imperfections or defects that are undesirable in fabricating integrated circuit devices or high conversion efficiency solar cells. Defects in single crystal silicon form in the crystal growth chamber as the crystal cools after solidification. Defects generally are classified as point defects or agglomerates (three-dimensional defects). Point defects are of two general types: vacancy point defects and interstitial point defects.

[10] In a vacancy point defect, a silicon atom is missing from one of its normal positions in the silicon crystal lattice. This vacancy gives rise to the point defect.

[11] An interstitial point defect occurs when an atom is found at a non-lattice site (interstitial site) in the silicon crystal. If the concentration of such point defects reaches a level of critical saturation within the single crystal silicon, and if the mobility of the point defects is sufficiently high, a reaction, or an agglomeration event, may occur.

[12] In a conventional CZ process, point defects are generally formed at the interface between the silicon melt and the solid silicon. Such defects arise, in part, due to thermal perturbations around the crystal resulting from convection currents and the inability to closely control and or maintain an optimal temperature distribution particularly in the solidification zone at the crystal/melt interface.

[13] Therefore, what is needed is an improved heating system with multiple separate heating zones to aid in controlling crystal formation rates and defect density. Also, such a configuration should substantially eliminate convection currents and thermal perturbations that lead to the formation of point defects. It also would be desirable to minimize the radiant energy that strikes the crystal during growth, allowing for more rapid cooling of the crystal and higher pull rates. In a conventional CZ process the hottest surface is that part of the crucible wall not submerged in the melt. A high aspect ratio crucible brings this surface in close proximity to the cooling ingot, inhibiting optimal cooling of the ingot largely through heating by radiation.

[14] Another problem with conventional CZ grown silicon is that it contains a substantial quantity of oxygen. This is due to the composition and configuration of the typical high-aspect ratio, narrow diameter crucible, wherein convection currents scrub the walls of the crucible and convey impurities into the melt and ultimately to the crystal itself. The convection currents add oxygen to the melt resulting from the slow dissolution of fused silica (silicon dioxide) on the walls of the crucible holding the molten silicon. This introduction of oxygen into the melt can cause defects in the finished crystal.

[15] In photovoltaic and other applications, high oxygen content in the silicon adversely affects minority carrier lifetime and greatly degrades performance and in photovoltaic devices reduces the conversion efficiency.

[16] Thus, what is needed is a crucible design that can minimize the introduction of

oxygen into the melt and provide substantially oxygen free silicon characterized by high minority carrier lifetime for photovoltaic and other applications. The use of a special coating or material for a crucible that would make the crucible resistant to breakdown by molten silicon currently is not feasible since the crucible is a single use item and is broken by solidification of unused silicon during the cool down period after each use.

[17] Therefore, what is also needed is a new crucible design that enables useful crucible lifetime to be extended over many cycles of operation without damage, and thus would make a potentially higher cost inert crucible surface economically feasible.

[18] Additional problems with a conventional CZ process are the inability to control dopant concentrations across the melt and across the resulting crystal. For many integrated circuit processes a desired dopant density is added to the silicon. Such dopant concentration is obtained by incorporating a small carefully controlled quantity of the desired dopant element, such as boron or phosphorus into the melt. For accurate control, a small quantity of heavily doped silicon is usually added to the undoped melt. The dopant concentration in the pulled crystal of silicon is always less than that in the melt because dopant is rejected from the crystal into the melt as the silicon solidifies. This segregation causes the dopant concentration in the melt to increase undesirably as the crystal grows. The seed end of the crystal therefore is less heavily doped than the tail end.

[19] The segregation effect is also a function of conditions including temperature. Thus, a non-uniform temperature distribution through the solidification zone, crystal/melt interface provides an undesirable dopant concentration gradient and attendant resistivity gradient along the crystal radius. Accordingly, what is also needed is a simplified crucible design that minimizes segregation and enables dopant concentration and resistivity to be substantially uniform throughout the crystal.

Technical Solution

[20] In order to overcome the foregoing disadvantages of conventional CZ processing systems, an aspect of the invention provides a system for continuous crystal growth comprising a low aspect ratio, large diameter, and substantially flat crucible, including an optional weir surrounding the crystal. The large diameter, low aspect ratio crucible substantially eliminates convection currents and reduces oxygen content in a finished single crystal silicon ingot. Multiple crystal pulling chambers are disposed with respect to the crucible, such that upon completion of crystal growth, a first pulling chamber moves a finished silicon ingot out of the growing zone for cooling, and a successive pulling chamber moves to position a new crystal in the growing zone, thereby eliminating down time associated with cooling the crystal and providing continuous crystal growth with high throughput.

[21] A separate level controlled silicon pre-melting chamber provides a continuous source of molten silicon to the growth crucible. This advantageously eliminates the

need for a crucible raising system and vertical travel of the growth crucible during the crystal pulling process, thus greatly simplifying the CZ crystal growing system. It will be appreciated that eliminating the need for vertical travel of the crucible and the crucible raising system enables controllable heater elements to be disposed across the base of the growth crucible in addition to heater elements disposed around the vertical walls.

Advantageous Effects

[22] The low aspect ratio crucible with annular heater elements disposed on the base advantageously provides a thermal distribution characterized by a low thermal gradient and small temperature difference between the walls of the crucible and the coolest spot at the center of the crystal in the solidification zone at the melt/crystal interface. Consequently the radial temperature gradient and convection velocity gradient across the solidification zone at the melt/crystal interface is significantly reduced providing uniform and optimal conditions throughout the solidification zone at the melt/crystal interface. Further, the region adjacent to the walls is no longer driven to an excess temperature. Thus, convection currents and thermal perturbations that are a chief cause of point defects are minimized again, contributing to uniform and optimal conditions.

[23] Minimized convection currents further reduce the quantity of oxygen introduced into the melt from scrubbing of the quartz crucible walls, enabling growth of crystals having fewer defects and lower oxygen content than is possible with a conventional CZ system. The continuous flow of molten silicon from the separate pre melting chamber coupled with the addition of dopant as needed during ingot growth permits compensation for segregation and establishes a substantially uniform dopant concentration axially (longitudinally) and radially in the grown crystal.

[24] The advantages of oxygen reduction achieved in the finished crystal, coupled with reduction in other impurities and reduction in dislocations in the crystal lattice, are especially useful for providing enhanced minority carrier lifetime for improved, high conversion efficiency photovoltaic devices.

[25] The low aspect ratio crucible increases the distance between the hot crucible wall not submerged in the melt and the cooling ingot, reducing heating by radiation and allowing optimal cooling of the ingot.

[26] Multiple crystal pulling chambers are rotatably or otherwise sequentially disposed with respect to the crucible, such that upon completion of a first single crystal silicon ingot, the first pulling chamber moves the finished silicon ingot out of the growing zone for cooling, and a successive pulling chamber moves to position a new crystal in the growing zone. The sequential positioning of pulling chambers at the growing zone completes the continuous process, eliminates down time associated with cooling each crystal and changing to a new crucible, and thus provides a system for continuous crystal growth with high throughput. Since in a continuous process the crucible and melt are not cooling and reheating to melt temperature, considerable energy savings

result. Also, the atmosphere around the heaters and crucible are not opened to ambient atmosphere, thus fewer impurities and contaminants are introduced into the crystal pulling chamber.

[27] Impurities introduced into the melt, e.g. from scrubbing action of convection currents within the crucible, are dependant upon the average dwell time of silicon in the crucible and the surface area of contact between the melt and the crucible, especially the surface area of the vertical walls of the crucible. In an aspect of the invention, the dwell time is minimized through the improved cycle time and the average area of contact is minimized through the optimized low aspect ratio crucible design. It will be appreciated that these same considerations will apply to the pre-melter whose sizing and therefore dwell time and surface area of melt contact are optimized.

[28] Another aspect of the invention provides enhanced temperature control that maintains a temperature in the melt of approximately 1420° C, such that the temperature has an optimized thermal distribution between the melt and crystal for accelerated crystal growth. To achieve such an optimized thermal distribution at the critical interface between the crystal and the melt, a plurality of annular, independently monitored heating elements are disposed in a radial pattern across the base of the growth crucible, as close to walls and to the bottom of the growth crucible as possible. The heating elements are separately controlled with active feedback to enable rapid thermal response and distribute the thermal workload to achieve an optimized thermal distribution across the interface between the crystal and the melt and between the crystal and walls of the crucible. This also contributes to improved crucible life, as well as reduction of oxygen and other impurities, in the finished single crystal silicon.

[29] In contrast to a conventional CZ system, the growth crucible is no longer a single use item, but rather can be reused over multiple crystal growing cycles. Accordingly, growth crucible surfaces in contact with molten silicon are provided with a coating of alpha or beta silicon carbide, or similar ceramic coating that is inert with respect to molten silicon and further safeguards against introduction of oxygen into the melt. It will be appreciated that for similar reasons the pre-melter can be fabricated from these advantageous materials.

[30] The foregoing aspects of the invention advantageously prevent the introduction of oxygen into the melt and provide a crucible that is capable of being used for about 10 crystal growing runs or more, while achieving a single crystal silicon product of substantially float zone quality with enhanced minority carrier lifetime. The oxygen reduction achieved in the finished silicon crystal is especially useful for providing enhanced minority carrier lifetime for applications such as improved conversion efficiency photovoltaic devices.

Description of Drawings

[31] The drawings are heuristic for clarity. The foregoing and other features, aspects and

advantages of the invention will become better understood with regard to the following descriptions, appended claims and accompanying drawings in which:

[32] **Figure 1A** is a schematic side view of a conventional CZ system.

[33] **Figure 1B** is a schematic side view of a conventional CZ system showing the undesirable temperature gradient through the melt.

[34] **Figure 2** is a schematic side view of a system for growing enhanced purity single silicon crystal in accordance with an aspect of the present invention.

[35] **Figure 3A** is a schematic side view of a crystal growing system showing a premelter and individually controlled heating elements in accordance with an aspect of the present invention.

[36] **Figure 3B** is simplified top view of the crystal growing system as shown in **Figure 3A** in accordance with an aspect of the present invention.

[37] **Figure 3C** is a schematic side view of the wide diameter, low aspect ratio crucible showing improved thermal gradient through the melt in accordance with an aspect of the present invention.

[38] **Figure 4** is a side view of a pre melter for a crystal growing system in accordance with an aspect of the present invention.

[39] **Figure 5** is a schematic diagram showing a system for heater control to establish an optimized thermal distribution across the crucible in accordance with an aspect of the present invention.

[40] **Figure 6** is a schematic diagram showing a system for level control in the crucible accordance with an aspect of the present invention.

Best Mode

[41] Referring to **Figures 1A** and**1B**, in a conventional CZ system pieces of polysilicon are melted in a fused silica crucible **100** in an inert atmosphere in growth chamber **102**. The atmosphere in the chamber **102** is typically argon and is controlled by isolation valve **104** in accordance with techniques that are well known. The silicon is held in crucible **100** at a temperature just above 1412 degrees C, the melting point of silicon. A high quality seed crystal with the desired crystalline orientation is lowered in the crystal pull chamber **106** to contact the melt at crystal melt interface **107** in the crucible **100** while being rotated. Crucible **100** is simultaneously rotated in the opposite direction to induce mixing in the melt and to attempt to minimize temperature non-uniformities. A portion of the seed crystal is dissolved in the molten silicon to remove strained outer portions and to expose fresh crystal surfaces.

[42] The seed is then slowly raised or pulled from the melt in crystal pull chamber **106** by conventional pull mechanism **108**. As the seed is raised, it cools and material from the melt adheres to it, thereby forming a larger crystal or ingot **103**. The main body of the crystal or ingot **103** is grown by controlling the pull rate and the melt temperature while compensating for the decreasing melt level in the crucible. That is, as the crystal grows, the molten silicon in the crucible **100** is depleted. In order to compensate for

the changing level of melt in the crucible **100**with respect to the heaters disposed around the vertical walls of the crucible, the crucible **100** must be elevated vertically in carefully controlled fashion from a starting crystal growth position **112** to a final or end position **114.**

[43] Complex mechanisms must be provided to coordinate the vertical travel of the crucible with the pulling of the crystal. The vertical travel of the crucible must be precisely coordinated with the pulling of the crystal in a vertical direction, such that a constant interface between the crystal and the melt is carefully maintained and the interface between the crystal and the melt is positioned correctly with respect to the heaters.

[44] The diameter of the crystal is controlled by decreasing or increasing its pull rate and/or the melt temperature until the desired or target diameter is reached. The initial pull rate is generally relatively rapid. The pulling continues until the melt is nearly exhausted. It is very expensive to design equipment that provides precise coordinated vertical travel of the crucible with the crystal pulling mechanism.

[45] **Figures 1A and 1B** show additional disadvantages associated with a conventional CZ crucible and heater arrangement. A conventional CZ crucible **100** is characterized by a narrow diameter, high aspect ratio. The high aspect ratio is necessary in order to hold all of the molten silicon for the growing crystal as there is typically no means for replenishment of the melt. Instead, the crucible **100** must travel in a vertical direction (from start position **112** to end position **114**) in coordination with the pulling of the crystal as silicon in the crucible is depleted.

[46] Heater elements **118** are provided around the circumference of the crucible **100** and produce a temperature distribution in the melt which disadvantageously maximizes the thermal gradient (DT) between the heater, the walls of the crucible, the melt and the crystal suspended in the center of the melt and can cause the walls of the crucible to be taken to excess temperatures. This disadvantageously slows crystal growth.

[47] In addition, convection currents are generated in the narrow diameter, high aspect ratio crucible **100.** Convection currents adversely affect the purity of the single crystal silicon. A conventional CZ crucible **100** is comprised of a material such a fused silica. Molten silicon breaks down the walls of a conventional fused silica crucible into silicon and oxygen. Convection currents scrub the walls of the crucible and convey oxygen and other impurities into the melt. This adversely affects the purity and defect structures in the growing crystal. Convection currents also create adverse thermal perturbations around the growing crystal that may induce defects into the crystal.

[48] Upon completion of crystal growth, residual molten silicon that is not removed from the crucible **100** greatly expands upon solidification and breaks the crucible. The typical CZ crucible **100** is therefore a single use disposable item that is discarded after each silicon ingot is grown.

[49] **Wide Diameter, Low-Aspect Ratio Crucible**

[50] Referring to **Figure 2**, a crystal growing system according to an aspect of the present invention provides a fixed, wide diameter, low-aspect ratio crucible **200** provided in growth chamber **202**, which is in turn provided with a base**201**. A conventional isolation valve **204** provides a vacuum or otherwise controls the atmosphere in growth chamber **202**and multiple crystal pull chambers**210a**and**210b** in a well-known manner. The wide diameter, low aspect ratio configuration of the crucible **200** is provided with a means for minimizing radiant heat, such as a heat shield **205**, for minimizing radiant energy that strikes the crystal or ingot **203** during growth. Heat shield **205** is a planar section of silicon carbide, graphite, or other high temperature material supportably mounted on the walls of the growth chamber **202** having an interior opening sized to accommodate the silicon ingot **203**. An annular region **211** adjacent the opening is deflected downward toward the melt to decrease heat flow along the ingot **203** and for minimizing thermal shock when the ingot is removed from the melt **222**.

[51] Referring to **Figure 3A**, an optional weir **220**is disposed in the melt **222** between the crystal /melt interface and outlet port **228** of silicon pre-melter **208**. The weir **220** rests on bottom of the crucible **200** or alternatively can be supported by support means such as any convenient supporting structure comprised of an inert material provided on the inner walls of the crucible. The top of the weir **220** extends above the surface of the melt **222**. The purpose of the weir is to enable molten silicon from the pre-melter **208** to be distributed into the melt without the formation of ripples in the melt or thermal perturbations that would disturb the temperature distribution in the melt and adversely affect the growing silicon crystal **224**. The weir **220** is characterized by low height in relation to its diameter and is generally cylindrical in shape with apertures provided in that portion of the weir extending beneath the surface of the melt to enable a desired thermal distribution in the melt.

[52] The wide diameter, low aspect ratio growth crucible **200** also prevents or greatly reduces formation of convection currents in the melt and attendant scrubbing action upon the crucible, further reducing the introduction of oxygen. In a preferred embodiment, the low aspect ratio (diameter with respect to height) of the crucible is in a range of 4:1 to 10:1 and preferably about 8:1. In contrast, conventional crucibles have aspect ratios on the order of about 1:1 - 1:4.

[53] Furthermore, annular heating elements are disposed in a radial pattern on or as close as possible to the base of the crucible, which was not possible in a conventional CZ grower due to the need for a lift mechanism. In addition to the heaters disposed around the circumference of the crucible, the annular heaters provide corresponding heating zones in the melt. This results in an optimal thermal distribution that is substantially horizontal through the melt. It also provides an optimal temperature distribution, particularly at the critical interface between the crystal and the melt. The improved temperature control provides accelerated crystal growth beyond what

previously has been possible.

[54] **Melting Of Granular Poly-Silicon In A Low Aspect Ratio Crucible**

[55] Conventional crucibles have high aspect ratios and lift mechanisms such that the level of the melt in the crucible, with respect to the heaters on the sides of the crucible, can be kept constant during crystal growth. Typically there are no heaters under the base of the crucible.

[56] When such crucibles are charged with poly-silicon material the temperature distribution during the melt down process is highly non-uniform. The temperature is highest closest to the walls of the crucible where it is closest to the heaters and also cooler at the top and bottom of the melting material than at the center. The problem is greatly exacerbated when the poly-silicon material is in granular form with small particles (<1mm diameter), large surface area and minimal points of contact between the granules, air being an excellent insulator. Heat flow between the granules tends to fuse them together at their points of contact. Additional heat flow is by radiation, very little is by convection at this stage. The granules closest to the heaters melt first and those at the edges and center slump down to the bottom of the crucible leaving a bridge of fused granules across the top surface and an air void beneath the bridge. Liquid silicon of course occupies much less volume than the granules. The combined effect is to retard the melting process and care must be taken not to drive melt temperatures close to the heaters to excess levels or contamination levels will increase. There are techniques to lessen the problem, but they are exacting and time consuming e.g. raising the crucible un stages up through the heaters such that the top of the mass of granules melts first, again being careful not to drive too much heat from the sides.

[57] Referring to **Figure 3B**, according to an aspect of the invention, a low aspect ratio crucible **200**, has a plurality of annular heaters **218** disposed in a radial pattern beneath its base in addition to side heaters **219**, to provide a much more uniform temperature distribution because of a) the lower depth of granules in the crucible and b) annular base heaters **218** applying heat in a more controlled distribution across the entire base surface area of the crucible. The annular base heaters **218** are preferably planar resistive heating elements that are individually controlled as described with respect to **Figure 5.** Each heating element **218** generates a corresponding heating zone in the melt to provide an optimal temperature distribution through the melt. The higher surface area of contact between the granules and the heated walls of the low aspect ratio crucible, compared to the high aspect ratio crucible, drives more heat into the granules. Thus, the entire mass of granules melts much more uniformly and at a much more rapid rate without the attendant contamination associated with excess temperatures close to the heaters.

[58] Referring to **Figure 3C**, a low aspect ratio crucible **200** with annular base heaters **218** develops a thermal gradient 223 characterized by a substantially horizontal distribution through melt **222.** In a continuous process using a low aspect ratio crucible,

compared to a batch process, it is easier to transfer the heat to melt the initial charge because of: a) a smaller amount of poly-silicon 'charge' melted at start-up and b) the pre-melter **208** providing liquid silicon to wet the granules provides larger areas of thermal contact between granules and accelerating the melting process. Note: the pre-melter also is designed to provide uniform heating around the granules rather than heating from one side to further enhance the melting process.

[59] **Pre Melter**

[60] Referring to **Figures 3A,4 and 5**, the pre-melter **208** comprises a separate containment vessel for melting a quantity of solid feedstock material and for providing a constant source of molten material to growth crucible **200** for growing crystals. In the case of single crystal silicon, a source **209** of solid silicon feedstock such as silicon chips, chunks, granules or rods is provided through flow control device **212** to the pre melter **208** at a rate sufficient to replenish the growth crucible.

[61] The pre melter can be separately situated apart from the growth chamber as shown in **Figures 5** and **6**. In a preferred embodiment, the pre melter **208** comprises a separate containment means provided within the growth chamber **202** for melting a quantity of feedstock and providing it to the surface of the melt **222**. This advantageously places the pre melter **208** in the controlled atmosphere of the growth crucible **222** and minimizes the distance that the melt from the pre-melter needs to travel needs to travel to reach the crucible.

[62] Referring to **Figure 4**, the pre melter comprises a melting chamber **400**. The pre melter is comprised of a quartz material capable of withstanding temperatures up to about 1590 degrees C. Fused silicon carbide, silicon nitride bonded silicon carbide or similar material also may be used for the pre melter. One or more resistive heaters **402** are suitably disposed beneath or adjacent the melting chamber for melting a quantity of solid crystalline feedstock. An optional thermal conductor **404** may bedisposed between the heaters **402** and melting chamber **400**. Thermal conductor **404** also is an electrical insulator. Thermal conductor **404** diffuses thermal flux from the heaters and reduces the maximum temperature seen by the quartz walls of the pre melter. Thermal conductor **404** also provides mechanical support for the quartz melting chamber at temperatures beyond about 1590 degrees C. Heaters optionally also may be disposed around the melting chamber.

[63] A source of dopant and solid silicon or crystalline feedstock **209** is provided through a flow controller **312** to an inlet **408** at or above silicon level **410** in a first section of the melting chamber **400**. A weir **414** defines a first portion or section **416** of the melting chamber including inlet **408**, and also defines a second section **418**, including an outlet to the crucible. The separate first section **416** of the melting chamber **400**, is provided with an inlet **408** for receiving the solid crystalline feedstock. Inlet **408** also provides a means for receiving a predetermined quantity of solid dopant material either directly or through the feedstock and dopant source **209**.

As a non-limiting example, dopant material can be a dice of heavily doped wafer on the order of 0.125x0.125x0.25 inches at a rate of up to 10 dices per ingot. Subsequent ingots in an ingot stream will require less dice. The amount of dopant dice required is a function of the amount of dopant taken up in the crystal as it is grown. That is, the dice simply top up that dopant which is taken up from the melt into the crystal. Adding dopant in the pre melter avoids thermal perturbations and non-uniform temperature distribution that otherwise would result from adding solid chunks of dopant into the melt. Such temperature distribution problems would arise from the latent heat of fusion and thermal capacity (mass x specific heat x D T) to bring the dopant material up to melt temperature. Note that such thermal perturbation problems are much the same as when adding solid silicon feedstock directly into the melt, although very much reduced. Due to the optimized thermal gradient across the melt and the control of thermal zones in the melt by respective individually controlled heating elements, a uniform thermal distribution can be maintained across the radius of the growing crystal. Thus, the addition of dopant material at inlet **408** can provide substantially uniform resistivity or conductivity axially (longitudinally) and radially in the finished ingot. First weir **414** is provided with a flow-controlling outlet **420** at the bottom of the first section **416.**

[64] Molten silicon enters the second portion **418** of melting chamber **400** from the bottom of the first section **416** through outlet **420.** The molten silicon then rises to the level **410** in the first section. Due to the fact that solid granules or unmelted pieces of silicon float, it is critical to provide a weir **414** in the pre melter to ensure that only molten silicon or crystalline feedstock circulates to the bottom of the first pre melter section **416** by means of the flow controlling outlet **420** of the weir and then fills the second section **418** from the bottom upward. The molten silicon or molten crystalline feedstock that enters the crucible melt from the outlet **424** is thus taken from the bottom of the pre melter. This arrangement advantageously ensures that unmelted, solid material, floating in molten silicon by virtue of its density lower than molten silicon, does not pass directly through to second section **418** of melting chamber **400** and on to the growth crucible.

[65] An outlet tube **424** also acts as a second weir and controls the melt level in melting chamber **400** of the pre-melter. Outlet tube **424** comprises a tube having an inlet for receiving molten crystalline feedstock from the second section **418** of melting chamber **400** and an outlet at its distal end that provides a substantially constant source for replenishment of molten crystalline feedstock to the melt in the crucible. Outlet tube **424** induces flow of molten crystalline feedstock along the interior thereof and into the melt in the growth crucible.

[66] Outlet tube **424** is characterized by an inner diameter of a sufficient size, approximately 1 cm, to overcome surface tension of the molten feedstock (surface tension of molten silicon is approximately 30 times greater than water). Surface

tension tends to stop or limit flow through the outlet tube for a given head of molten crystalline feedstock in the pre melter. Thus, the diameter of the tube is optimized to overcome surface tension, while at the same time minimizing the splash effect that would cause excessive perturbation in the melt in the crucible. The distal end of the outlet tube is positioned at a point above the level of melt in the crucible, at a height chosen to minimize perturbations when discharging molten feedstock and dopant into the melt for continuous replenishment of the crucible. The design of the outlet tube thus further maintains static thermal conditions at the crystal melt interface that result in substantially uniform axial (longitudinal) and radial resistivity or conductivity in the finished ingot.

[67] In this manner pre-melter **208** provides a substantially constant source of molten silicon to growth crucible **200,** replenishing the silicon that is being taken up by the growing crystal. This enables the melt in growth crucible **200** to be maintained at a constant level with respect to a growing crystal, without the need for vertical travel of the crucible and also enables the level of the melt in the crucible to be increased or decreased as required. This advantageously eliminates the complex mechanisms in a conventional CZ system necessary for coordinating vertical travel of the crucible with the pulling of the crystal. Such replenishment by the pre melter also enables heaters to be positioned on the base of the crucible. This aspect of the invention greatly simplifies the apparatus needed for growing single crystal silicon and ultimately enables accelerated production of single crystal silicon at lower cost.

[68] The substantially continuous addition of melted silicon by the use of pre melter **208** eliminates the lost time involved and energy wasted in shutting the furnace or heating elements off to recharge the crucible **200** and remelt the silicon. The use of a substantially continuous source of molten silicon feedstock to replenish the melt minimizes the time the melt is in contact with the crucible, thus further limiting oxygen absorption into the melt. Since the raw silicon is melted within the pre-melter in very small quantities and immediately flows into the growth crucible, dwell time and surface area of contact are likewise minimized. Furthermore, there is no need to open the growth chamber to ambient atmosphere in order to replace the crucible and provide a new silicon charge, a process introducing new contamination into the growth chamber.

[69] Another advantage of silicon pre-melter **208** is that the axial resistance of the crystal can be better controlled as dopant can be added during recharging. This advantageously eliminates the axial resistivity gradient exhibited in crystals grown by the conventional CZ process. The effects of segregation in the melt and resulting non-uniform dopant profiles in the crystal are substantially eliminated. Yet another advantage of using a separate silicon pre-melter **208** communicating with growth crucible **200** is that eliminating the high temperature initial melting of a silicon charge minimizes the stress on the growth crucible and lowers the precipitation of oxygen into

the melt.

[70] It will be appreciated that the pre-melter can be made from, or coated with, an inert material such as sintered silicon carbide or like ceramic, or with other materials characterized by an inert character with respect to molten silicon such as tantalum, niobium, or oxides and compounds thereof, to reduce oxygen and other impurities in the melt, as is the case for the crucible.

[71] The silicon pre-melter 208 in combination with the low aspect ratio, non-reactive, sintered silicon carbide crucible 200 and controllable dopant feed during crystal growth substantially eliminates segregation, high impurity levels and oxygen precipitation that cause defect structures and sites of minority carrier recombination. This aspect of the invention is especially useful in providing higher minority carrier lifetime silicon for high conversion efficiency solar cells.

[72] Multiple Crystal Pulling Chambers

[73] Referring again to **Figures 2** and **3A**, multiple pull chambers **210a, 210b** are provided on a rotating cylinder **212** that is in turn supported by a spindle **214**. It will be appreciated that multiple pull chambers **210a, 210b** also can be arranged in a moveable, linear supporting member for consecutive positioning of a seed crystal in each successive pulling chamber into the growth zone in crucible **200**within growth chamber**202.** Multiple pull chambers **210a, 210b** thus are rotatably or sequentially disposed with respect to the growth chamber **202**. Upon completion of a first single crystal silicon ingot, the first pulling chamber **210a** moves the finished silicon ingot out of the growing zone in crucible **200** and out of growth chamber **202** for cooling, and a successive pulling chamber **210b** moves to position a new crystal into growth chamber **202** and to the growing zone at a crystal / melt interface in crucible **200**. The isolation valve **206** closes to control the atmosphere in growth chamber **202**and the associated pull chamber, and a new crystal is grown.

[74] The sequential positioning of pulling chambers **210a, 210b** at the growing zone in crucible **200** ,is the final step in the continuous process,minimizing dwell time of silicon in the growth crucible, eliminating down time associated with cooling each crystal, changing to a new crucible, recharging the crucible, evacuating the growth chamber and reheating the charge to melt temperature; thus providing an accelerated, continuous crystal growth system with high throughput. Also, such a continuous process eliminates the single use nature of the growth crucible and enables the growth crucible to be used for multiple (10 or more) crystal growing cycles.

[75] **Composition of Crucible**

[76] Referring again to **Figures 2, 3A, 3B** and **3C** , another aspect of the invention provides a low aspect ratio, wide diameter crucible **200** comprised of a material that is inert to molten silicon such as alpha or beta sintered silicon carbide, tantalum nitride, or similar ceramic that contains no silica. Alternatively, the interior silicon containing surface of the crucible **200** may be provided with a coating of such an inert material in

accordance with techniques that are well known. Such a desirable inert material is comprised of a mixture of silicon carbide grains and a sintering aid that is pressed and sintered. Unlike reaction-bonded carbide, there is no free silicon present. Such direct sintered materials have no metal phase and are therefore resistant to chemical attack. Alpha silicon carbide refers to a hexagonal structure and beta to a cubic structure.

[77] Such sintered silicon carbide materials are available from CARBORUNDUM Corp., designated SA-80; from GENERAL ELECTRIC, designated as Sintride, and from KYOCERA, designated as SC-201.

[78] A chemically inert growth crucible **200** comprised of the foregoing sintered silicon carbide materials is unknown in a conventional CZ growing process, because the conventional crucible is a single use, disposable item, and there is no motivation to provide a sintered silicon carbide or ceramic crucible or such a coating on the crucible surface.

[79] A conventional CZ growing process does not contemplate the use of a crucible material, such as sintered silicon carbide, to substantially eliminate the introduction of oxygen into the melt. In a conventional CZ system, a growth crucible is typically discarded after one or two growth cycles. Thus, a coating of silicon carbide or a crucible made from a higher cost material would add significantly to the cost of a conventional CZ system. It will be appreciated that these materials can also be used advantageously in the pre-melter for similar reasons.

[80] Further, oxygen precipitates originating from the growth crucible walls previously were not recognized as a serious problem and even could be beneficial in integrated circuit and other electronic devices. Oxygen precipitates form sites on which other impurities tend to accumulate. Such oxygen precipitates can be positioned in a predetermined manner remotely from an active device region in a finished IC wafer. Oxygen precipitates then function as gettering sites that attract unwanted impurities away from electrically active regions, thereby improving device performance.

[81] However, in accordance with an aspect of the invention, oxygen precipitates and associated defects are recognized as a problem for minority charge carrier lifetime in silicon that is to be used for specialized applications such as solar cells. In a solar cell, if some of the generated carriers in a photovoltaic cell recombine at defects, impurities, or sites of oxygen precipitates in the silicon, before reaching the electrical contacts, output current is diminished. Across multiple solar cells, such defects can seriously decrease output current.

[82] **Heater and Melt Temperature Control**

[83] **Figures 3B, 3C** and **5** show a heater and melt temperature control system that provides closed loop control of temperature characterized by optimal temperature distribution across the melt and uniform optimal thermal conditions in the solidification zone at the melt / crystal interface **207** aiding in controlling crystal formation rates and further minimizing defect density.

[84] Referring to **Figures 3B** and **5**, a plurality of annular resistive heating elements **218** are disposed in a radial pattern beneath the low aspect ratio crucible **200**. Additional resistive heating elements **219** are disposed around the circumference of the outer wall of crucible **200**. Annular heating elements **218** and sidewall heating elements **219** are individually controlled by heater control **240** to generate separate heating zones for providing an optimal temperature distribution across the melt. Heater control **240** includes a microprocessor controller for controlling and monitoring the activation time, power consumption and consequently thermal output of each heater element in response to signals from the sensors **234**.

[85] A desired thermal output can be maintained for each separately controllable resistive heating element to thereby achieve optimal temperature distribution across the melt and across the radius of the growing crystal. The desired thermal output and resulting temperature distribution are derived by measuring the power consumption of each of the individually controllable resistive heating elements through the microprocessor of heater control **240**. Power consumption of each heater corresponds to the thermal output needed to achieve the optimal temperature distribution. Heater control **240** applies power to each heater element in accordance with the monitored power consumption to achieve a repeatable state such that the corresponding thermal zones drive heat uniformly into the melt. It is to be understood that the advantageous heater arrangement and controllable thermal zones also can be used to drive heat uniformly into a molten material that includes solid granules. The heater arrangement also can be applied to uniformly heat and melt solids, such as granules, a combination of granules and chips, as well as chips or chunks of solid crystalline feedstock. With the optimal arrangement of independently controlled heaters underneath the low aspect ratio crucible, the thermal path into the charge across the contact points between the pieces of solid material is minimized. This is especially important when small chips or granules are used, as these have many more points of contact between adjacent chips or granules for a given mass or material, thus reducing or limiting heat flow. This effectively provides both a higher surface area of contact and shorter thermal path into the charge in the crucible, including solid material.

[86] This overcomes problems in conventional CZ systems wherein solid material, especially small chips and granules, closest to the heaters melt first and those at the edges and center slump down to the bottom of the crucible leaving a bridge of fused granules across the top surface and an air void beneath the bridge.

[87] Thus, a series of thermal zones representative of an optimal thermal distribution are established across the melt. Each thermal zone corresponds to the thermal output of a separately controlled resistive heater element **218**. A temperature sensor **234** comprising one or more optical pyrometers takes a temperature reading of each separate thermal zone across the melt, each zone controlled by a corresponding heater element. A single pyrometer also may scan separate zones, providing an output signal

on lead **236** representative of the temperature of each zone. The temperature sensor **234** also may include a thermocouple for sensing temperature of the outer heating elements **219** disposed around the circumference of the crucible **200**.

[88] In accordance with standard closed loop load regulation techniques, the temperature sensor **234** sends a signal on line **236** representative of the temperature of each respective thermal zone to heater control unit **240**. Heater control unit **240** sends a corresponding activation signal to each heating element to maintain that heating element in a predetermined range. After achieving the desired control set point, heater and melt temperature can be maintained in a narrow range. It will be appreciated that individual control of resistive heating elements **218** provides an optimized thermal distribution between the walls of the crucible and the crystal. The rate of pull (rate of growth of the crystal) is controlled by the temperature distribution at the interface between the crystal and the melt. Accordingly, this aspect of the invention provides an optimized temperature distribution to be maintained substantially horizontally across the melt and particularly at the crystal melt interface with greater control than was previously possible. It will be appreciated that this optimized temperature distribution is achieved by the unique design of the wide aspect ratio crucible in combination with the individually controlled heating elements placed beneath and around the crucible coupled with the lower depth of melt.

[89] Referring again to **Figure 4**, since introduction of solid silicon feedstock into the melt can cause temperature perturbations, improved control of the melt is achieved by silicon pre-melter **208** wherein the predominance of all melting of silicon is done outside the crucible. A source of solid silicon feedstock **209** comprises silicon feedstock in a variety of forms such as crushed silicon, chips, chunks, granules from a fluidized bed, silicon rods, or the like.

[90] As shown in **Fig 5**, a predetermined diameter of the crystal **244** can be closely controlled with active feedback. A meniscus sensor **232** comprising a camera or similar photo-detector system is used to monitor the diameter of the crystal as it grows using conventional optical pattern recognition techniques. Crystal growth takes place at the meniscus interface 207 between the crystal **244** and the melt **222** and the pull rate is adjusted to give the desired ingot diameter. In this way, a predetermined crystal diameter and crystal growth rate may be closely controlled with active feedback.

[91] Level Control

[92] Referring to **Figure 6**, in a preferred embodiment, improved level control of the melt **222** in the growth crucible **200** and the rate of discharge of molten silicon feedstock from pre-melter **208** into the melt **222** is achieved by an active feedback system for sensing the weight of the silicon melt in the growth crucible and adjusting the amount of silicon feedstock provided to the pre melter, and the amount or rate of molten silicon discharged from the pre melter **208** into the melt.

[93] A sensitive means for determining the weight of the growth crucible both empty

and with a desired level of melt is provided by a weight sensor **300.** A suitable weight sensor **300** comprises one or more strain gauge based load cells. Each load cell is a transducer that converts a load or weight acting on it into an electrical signal representative of that load. The weight of silicon melt in the crucible **200** produces a deflection of a mechanical beam or arm **304** that is in contact with the crucible **200.** This in turn produces an electrical resistance change proportional to the load. The load cell or weight sensor **300** then produces an output signal representative of the weight of the melt **222** to microprocessor based level controller **306** over a communication link **308.** The communication link **308** can be can be an electrical cable or a fiber optic, infra red or wireless link to provide stable high temperature operation.

[94] In response to signals from weight sensor **300,** level controller **306** produces output signals over a communication link **310** to actuate a dispenser or flow controller **312** that controls the release of a predetermined amount of solid silicon feedstock **209** into the pre melter **208.** Level controller **306** comprises a microprocessor for determining output of the pre melter based on a desired depth D of melt in the growth crucible. According to an aspect of the invention, this is determined by the following relationship:

[95] $D = (W - Wt) / (p R^2 r)$

[96] where W is the total weight of the crucible **200** containing melt **222;** Wt is the weight of the crucible **200** measured empty; R is the internal diameter of the crucible; and r is the density of liquid silicon.

[97] In this manner, it is possible to control the level of the silicon in the pre melter and the level of the melt **222.**

[98] It will be appreciated that the foregoing system provides an optimal output capacity of the pre melter and enables a closely controlled, optimized replenishment of the pre melter and growth crucible. This advantageously accelerates throughput by allowing crystal growth to be run with a much lower charge of melt than in a conventional CZ process and contributes to the reduced dwell time of the silicon in the crucible and attendant reduction in impurities. This further enables a new crystal to be started more quickly after emptying the crucible through a combination of crystal growth and truncating flow from the pre melter.

[99] The foregoing features of the present invention provide a single crystal silicon growth process that minimizes the precipitation of oxygen into the melt and minimizes or eliminates impurities and segregation in the melt. Because those factors minimize impurity levels and defect structures that give rise to carrier recombination sites, the process of the invention directly achieves enhanced minority carrier lifetime in silicon. Such silicon with enhanced minority carrier lifetime also can be achieved at higher growth rates and lower cost than were previously possible, due to the simplified crystal growing apparatus. The silicon produced by the process according to this invention has a particular advantage in providing more efficient, low-cost high lifetime solar cells.

Industrial Applicability

[100] **Scope**

[101] While the invention has been described in connection with what are presently considered to be the most practical and preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments and alternatives as set forth above, but on the contrary is intended to cover various modifications and equivalent arrangements included within the scope of the forthcoming claims. For example, other materials that are amenable to being grown by the CZ process may be employed as the melt material, such as gallium arsenide, gallium phosphide, sapphire, and various metals, oxides and nitrides. Also, other materials that are resistant to breakdown by molten silicon, such as ceramic coatings, or various metals, oxides, nitrides, and combinations thereof can be used for the composition of the crucible, or as a coating on interior walls of the crucible.

[102] Separate weirs or baffles can be provided to protect the crystal from convection currents and thermal perturbations. Multiple pulling chambers can be provided for continuous pulling of successive crystals without necessarily being rotated in place over the crucible. What is important is that a succession of crystal pulling chambers are sequentially positioned over the crucible for repeated, substantially continuous crystal growth without the need to remove the crucible after each growth cycle. Therefore, persons of ordinary skill in this field are to understand that all such equivalent arrangements and modifications are to be included within the scope of the following claims.

Sequence Listing

[103]